largely in place, the stage seems set for an exciting revitalization of analytical ultracentrifugation as the cell biologists begin to tackle the characterization of the myriads on interactions detected during the past few decades of qualitative research.

See also: **II/Centrifugation:** Analytical Centrifugation, Theory.

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Preparative Centrifugation

See **II/CENTRIFUGATION/Large-Scale Centrifugation**

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Theory of Centrifugation

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Introduction

Separation

Separation, as discussed here, is a mechanical means of the following:

- Separating immiscible liquids with different specific gravities (purification).
- Removing insoluble solids from a liquid (clarification if a liquid is the main product; dewatering if the solids are the chief product).
- Removing excess liquid from insoluble solids (thickening with the solids slurry in a more viscous form being the product).
- Some intermediate combination (degritting – removal of oversize particles; desliming – removal of fine particles; or some other form of classification – splitting the slurry into two generally liquid components with the solids being split based on particle size and/or density).

Centrifuges

Centrifuges are usually divided into two types, sedimenting and filtering. Sedimenting centrifuges are characterized by a solid bowl wall and include tubular bowl (**Figure 1**), disc stack (**Figure 2**) decanter (**Figure 3**) and imperforate basket centrifuges. Filtering centrifuges have perforated bowl walls, which support screens or cloth or both and include perforate basket centrifuges, peelers and pushers.

The ultracentrifuge and the gas centrifuge represent special cases that establish separations based on gradients on a molecular scale and are not included in this discussion.

Although centrifuges have been applied industrially for well over a century, centrifuge theory is not well developed. Centrifuges are not designed for specific applications using fundamental principles. Any discussion of centrifuge theory must also define the limitation of the theory. The best means of predicting the performance that will be obtained by processing a material through a centrifuge is to actually process the material through a centrifuge.

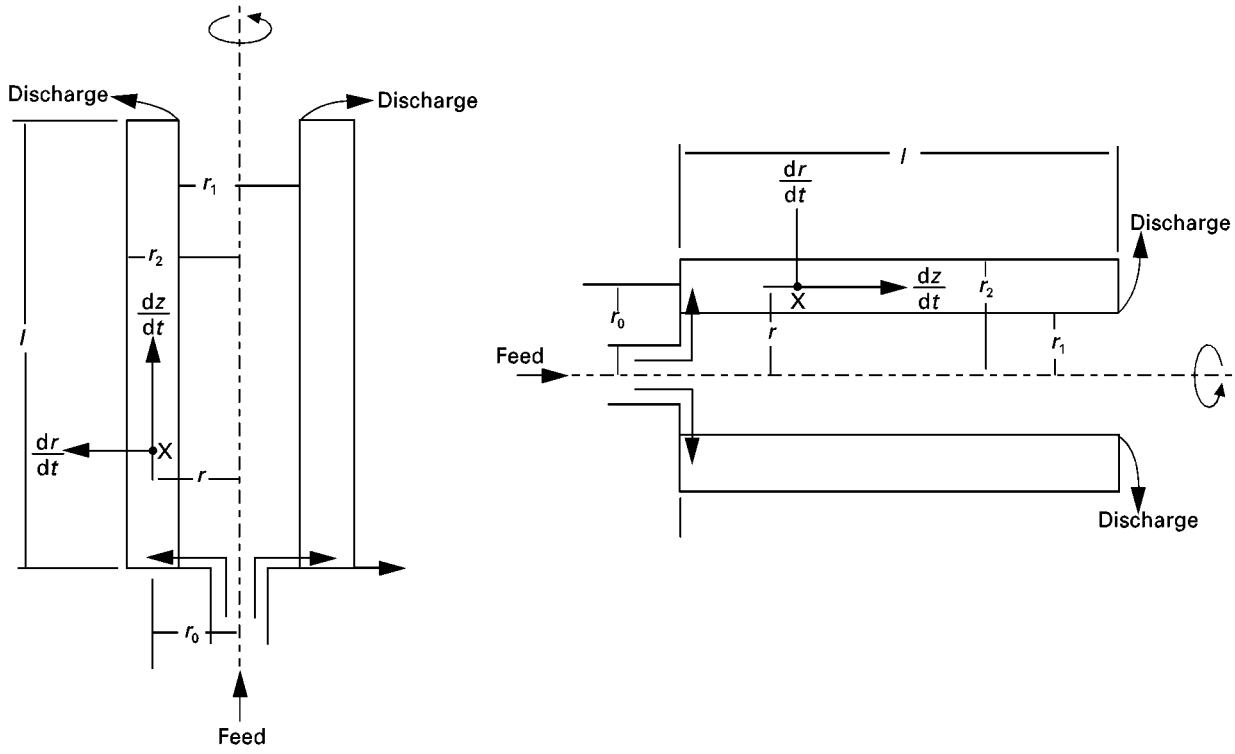

Figure 1 Tubular bowl (X represents the initial position). Centrifugal field is high enough that separating capacity of bowl is considered the same when rotating vertically or horizontally. Same sigma formula applies to tubular bowl, decanter and imperforate basket.

G-level

The fundamental characteristic of all centrifuges is that they contain a rotor that spins. A centrifugal field is used to augment separation. The magnitude of the enhancement is sometimes incorrectly described as the G-force. The relative centrifugal force (RCF) or G-level is not a force; it is a ratio, that of acceleration of the centrifugal field to that of acceleration owing to the Earth's gravity. It has dimensionally no units:

$$G = \omega^2 r/g \left(\frac{1}{s^2} \times \text{cm}\right)/(\text{cm s}^{-2}) \qquad [1]$$

This ratio may reach 60 000 on small laboratory units and 20 000 on small industrial scale units. This ratio tends to decrease as the size of the rotor increases. The ratio is normally large enough that a rotor rotating horizontally is considered to have the same separating capacity that it would have if it rotated

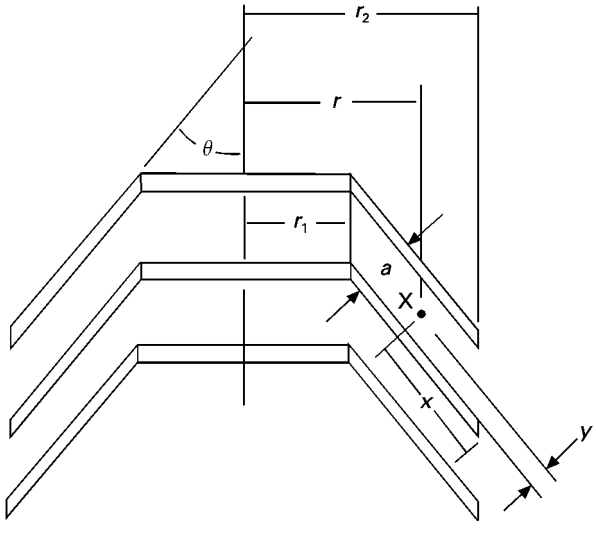

Figure 2 Disc centrifuge (X represents the initial position).

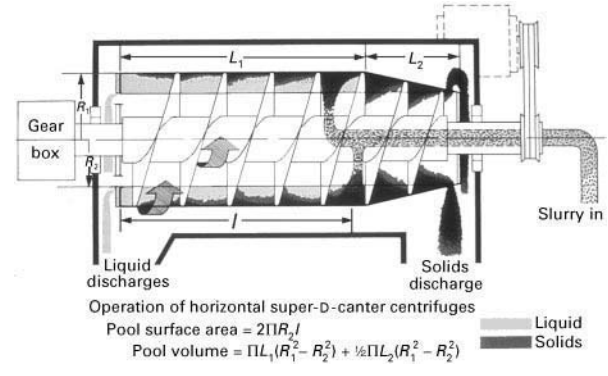

Figure 3 Decanter.

vertically, i.e. the influence of the Earth's gravitational field is negligible while the rotor is spinning.

Performance

Since centrifuges typically remove solids from one or more liquid streams, some measure of how well this is being performed is usually desirable. The recovery, sometimes (especially in the case of filtering centrifuges) referred to as yield, is defined as:

$$\text{Recovery (\%)} = \frac{\text{Collected insoluble solids}}{\text{Feed insoluble solids}} \times 100 \quad [2]$$

$$= \frac{\text{Cake insolubles (\%)} \times \text{Cake rate}}{\text{Feed insolubles (\%)} \times \text{Feed rate}} \times 100 \quad [3]$$

$$= \frac{cC}{fF} \times 100 \quad [4]$$

As a practical matter, cake rates are difficult to measure. This can be addressed by manipulating mass balances. Recovery can be defined in terms of insoluble (suspended) solids concentrations, which may be more accurately determined than cake rates.

The liquids balance:

$$F = C + E \quad [5]$$

or:

$$E = F - C \quad [6]$$

The solids balance:

$$fF = cC + eE \quad [7]$$

By substitution:

$$fF = cC + e(F - C) \quad [8]$$

$$= cC + eF - eC \quad [9]$$

$$F(f - e) = C(c - e) \quad [10]$$

$$C/F = (f - e)/(c - e) \quad [11]$$

$$\text{Recovery (\%)} = (c/f)((f - e)/(c - e)) \times 100 \quad [12]$$

Recovery then is also a function of feed solids concentration. Effluent quality is not the sole measure of recovery. High solids concentration in the effluent may simply mean that the feed solids are high. Conversely, lack of solids in the effluent may simply mean lack of solids in the feed, not a high level of recovery.

The use of overall percentage recovery may not be adequate to compare dissimilar centrifuges, especially those on applications such as classification when recovery levels are kept low.

Centrifuges may have the effect of altering the particle-size distribution. Two different types of centrifuges, even if operating at the same overall recovery level, may split a slurry into components having significantly different particle-size distributions.

Sedimenting Centrifuges

Ideal System

Newton and Stokes have promulgated the laws describing the movement of particles. When a force is applied to a particle it is accelerated:

$$F = ma \quad [13]$$

In a static settling tank under the influence of the Earth's gravity, the particle settles along the radius of the earth. When g is the gravitational constant:

$$F = mg \quad [14]$$

In a centrifugal field, the acceleration, $\omega^2 r$, results in a force that acts normal to the axis of rotation (**Figure 4**):

$$F = m\omega^2 r \quad [15]$$

In a sedimenting centrifuge, a continuous liquid phase moves through the rotor. In order to accomplish a useful separation, the discontinuous phase – either the insoluble solids or immiscible liquids drops (or both) – must move in a direction different from the flow of the continuous liquid. Stokes' law is usually applied to describe the relationship. The effective force accelerating the particle in a centrifugal field is then described:

$$F_p = (m_p - m_1)\omega^2 r \quad [16]$$

where m_p is the mass of the particle and m_1 is the mass of the liquid displaced by the particle. If we define $\Delta\rho = (\rho_p - \rho_l)$, the difference in the density between the particle and the continuous liquid phase, then for a spherical particle of diameter, D:

$$F_p = (\Pi/6)\Delta\rho D^3 \omega^2 r \quad [17]$$

If the diameter is small, or the viscosity is high, the particle moves at a velocity below the turbulent range and Stokes' law defines the force of the liquid phase

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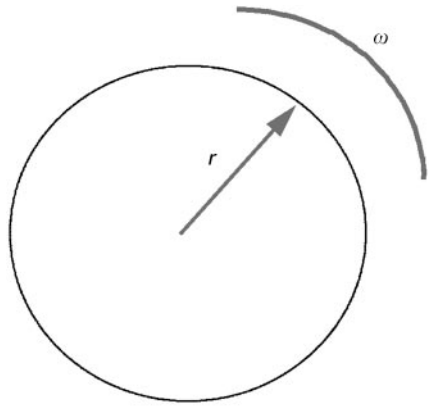

Defined as:

$$\frac{\omega^2 r}{g}$$

where :
ω is rotational velocity (rad s^{-1})
r is radius of rotation in inches
g is gravitational constant (32.2 in s^{-2})

Figure 4 G-level.

resisting the particle as:

$$F_l = 3\Pi\eta D v_s \qquad [18]$$

If the particle settles long enough (reaches equilibrium), then $F_l = F_p$ and, in a centrifugal field:

$$v_s = (\Delta\rho D^2\omega^2 r)/18\eta \qquad [19]$$

In the Earth's gravitational field:

$$V_g = (\Delta\rho D^2 g)/18\eta \qquad [20]$$

The difference between the velocity in the centrifugal field and in the Earth's gravitational field is twofold. The first difference is that the velocity in the centrifugal field may be three to four orders of magnitude higher. The second is that the velocity in a centrifugal field depends on the distance from the centre of rotation, so that the velocity increases as the particle moves outward from the centre of rotation. In the Earth's gravitational field, the velocity is considered independent of position.

Sigma Value

The most widely used method of quantifying capacity in sedimenting centrifuges is the sigma value which was introduced by Ambler in the 1950s. Sigma is used as an index of centrifuge size and typically has units of cm^2.

The sigma concept attempts to isolate the process system factors effecting separation from the centrifuge factors effecting separation (Figure 1). The tubular bowl was the first centrifuge to which sigma is applied. The tubular bowl is a rotating cylinder in which feed is introduced through the bottom end cap. The continuous fluid flows through the rotor and overflows the top of the bowl. If the solid particles having a specific gravity higher than the liquid are successfully separated, they accumulate on the inside of the rotor and are removed batchwise by manually cleaning the bowl. If the distance settled (x) is small, the velocity is constant, eqn [19] then can be expanded:

$$x = v_s t = [(\Delta\rho D^2\omega^2 r)/18\eta](V/Q) \qquad [21]$$

If we consider an ideal system, half of the particles of diameter D would be removed when:

$$x = s/2 \qquad [22]$$

$$Q = [(\Delta\rho D^2)/9\eta](V\omega^2 r/s) \qquad [23]$$

or:

$$Q = 2v_s\Sigma \qquad [24]$$

where v_s characterizes the process system:

$$v_s = (\Delta\rho D^2 g)/9\eta \qquad [25]$$

and Σ characterizes the centrifuge:

$$\Sigma = (V\omega^2 r_e)/g s_e \qquad [26]$$

with r_e and s_e being the effective radius and effective settling distance in the centrifuge.

The problem then is to define r_e and s_e. If the liquid layer is not thin, Ambler considered that:

$$r_e/s_e = 1/\ln(2r_2^2/r_2^2 r_1^2) \qquad [27]$$

Ambler maximized the approximation for the tubular bowl as:

$$\Sigma = (2\Pi l\omega^2/g)(\tfrac{3}{4}r_2^2 + \tfrac{1}{4}r_1^2) \qquad [28]$$

Svarovsky and Vesilind each use slightly different approximations for the effective radius.

Records argues that a second derivation assuming that all particles start on the surface instead of uniformly distributed throughout the annular space yields:

$$\Sigma = (2\Pi l\omega^2/g)(\tfrac{1}{2}r_2^2 + \tfrac{1}{2}r_1^2) \qquad [29]$$

Clearly as the depth of liquid decreases $r_1 \to r_2$, the values for both estimates of Σ become equal.

The equivalent area of a decanter and a gravity settling tank is shown in **Figure 3** and **Figure 5**, respectively.

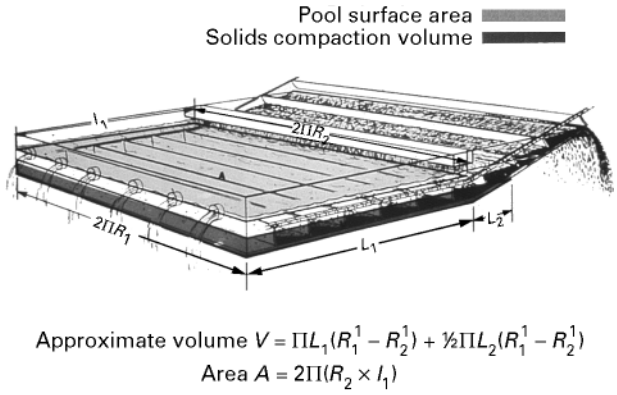

Figure 5 Gravity settling tank.

Sigma assumptions The assumptions can be divided as follows:

- *Stokes' law*: The particles or droplets are spherical and uniform in size. Settling of a particle is unhindered by the smaller particles ahead of it. The particles do not deaggregate, deflocculate, agglomerate, precipitate, dissolve, emulsify or flocculate. There is no change in viscosity or density (little or no temperature change).
- *Reynolds' number*: The value for the Reynolds' number, $(v_s\rho D)/\eta$, is less than one, so that the deviation from the Stokes settling velocity is relatively small.
- *Distribution*: The particles are evenly distributed in the continuous liquid phase. The feed is uniformly introduced into the full space available for its flow. The flow is streamlined. There is no displacement of flow of the continuous phase by the sedimented particle phase or the introduction of feed. There is no remixing of the continuous and discontinuous phases.

Sigma limitation: similarity of feed Since Σ is the index of the size of the centrifuge, traditionally the throughput (Q_1) of a centrifuge of a size (Σ_1) has been used to determine the throughput (Q_2) to a usually larger size (Σ_2) centrifuge. In the normal course of commerce, the performance of the test centrifuge with Σ_1 occurs at a time and place different from that in which the centrifuge with Σ_2 will operate. The small unit may be tested on lab batches, months or even years ahead of the construction of a full-scale plant. Eqn [24] can be restated as:

$$Q_1 = 2v_{s1}\Sigma_1 \qquad [30]$$

and:

$$Q_2 = 2v_{s2}\Sigma_2. \qquad [31]$$

It is important to remember that:

$$Q_2 = Q_1(\Sigma_2/\Sigma_1) \qquad [32]$$

if and only if:

$$v_{s1} = v_{s2} \qquad [33]$$

The process system parameters that allow v_{s1} must be duplicated to allow v_{s2}.

The feed stream and process system should be properly documented to ensure that the process system does not adversely effect the following properties described in eqn [25]:

$$v_s = (\Delta\rho D^2 g)/9\eta$$

It is generally assumed that increasing the sedimenting velocity (v_s) produces a better (more complete, faster, possibly more economical) separation. Therefore increasing v_s increases sedimentation capacity at constant Σ. Eqn [14] illustrates several important relationships:

- The larger the particle diameter, the greater the sedimentation rate.
  Corollaries:
  A. Flocculation may enhance performance by increasing particle size.
  B. Care should be taken in those process steps ahead of the centrifuge to limit particle-size degradation by either mechanical or biological means.
- The greater the difference in the density between the particle and the continuous phase, the greater the sedimentation rate.
  Corollaries:
  A. Temperature is important. If the density differences are small, the percentage change in density of the continuous phase may be significant. The density of water is normally taken as unity, but actually changes by approximately 20% from 20°C to 30°C.
  B. In certain systems, e.g. mineral oil and water, there may be no density difference at a given temperature, therefore separation would not be possible. Changing the temperature and thus the densities would make separation possible. In extreme cases, changing the temperature may invert the light and heavy immiscible phases.
- The lower the viscosity of the continuous phase, the greater the sedimentation rate.
  Corollaries:
  A. Again, temperature is important. Warmer (not approaching the boiling point, and in the absence of significant increases in the solubility of the particles) is generally better than colder.

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B. Materials such as tar, that may be solid at room temperature, may be liquid with a low enough viscosity for processing at elevated temperature.

Parameters such as the speed of the feed tank agitator, the type of feed pump impeller, and ambient cooling owing to seasonal temperature fluctuations, may adversely impact the separation. In biologically active systems, factors such as differences in pH, alkalinity or volatile solids may indicate a difference in the feed stock to the separation system.

Sigma limitation: efficiency The sedimentation that the sigma value attempts to quantify is only a portion of the task to be accomplished. By assumption, sigma allows comparison of centrifuges which are geometrically and hydrodynamically similar. In practice, an efficiency factor is often introduced to extend the use of sigma to compare dissimilar centrifuges. Therefore we can expand eqn [21]:

$$Q_2 = Q_1(\Sigma_2/\Sigma_1)(e_2/e_1) \qquad [34]$$

again, if and only if $v_{s1} = v_{s2}$.

If the two centrifuges are geometrically and hydrodynamically equal, the efficiency factors cancel. Axelsson has attempted to quantify the efficiency of the various types of sedimenting centrifuges and has provided the data in **Table 1**.

Scale-up The sigma formula for the various types of imperforate centrifuges are listed in **Table 2**.

When testing a new material for separability on a centrifuge, a bottle centrifuge (**Figure 6**) is usually used to estimate the G-level required. To estimate size from the bottle centrifuge:

$$Q_B/\Sigma_B = (2g/\omega^2 t)\ln(2r_c/(r_c + r_1) \qquad [35]$$

By adapting eqn [34], the full-scale centrifuge (Σ_L) for the full-scale flow (Q_L) can be determined:

$$(Q_L/Q_B) = (\Sigma_L/\Sigma_B)(e_L/e_B) \qquad [36]$$

$$\Sigma_L = \Sigma_B(Q_L/Q_B)(e_B/e_L) \qquad [37]$$

where $e_B = 1$ and e_L is between 0.5 and 0.9.

Table 1 Efficiency of various types of sedimenting centrifuges

Sedimenting centrifuge type	*Efficiency factor (e)*
Disc stack	45–73%
Decanter	54–67%
Tubular bowl	90–98%

Table 2 Sigma formula for the various types of imperforate centrifuges

Centrifuge type	*Sigma formula*
Bottle centrifuge	$\omega^2 V/2g[r_c/(r_c + r_1)]$
Imperforate bowls (tubular, decanter, basket)	$2\Pi l(\omega^2/g)(\frac{3}{4}r_2^2 + \frac{1}{4}r_1^2)$
Disc stack	$(2\Pi n\omega^2/3g)(\cot\Theta(r_2^3 - r_1^3))$

The sizing should then be confirmed by testing the selected centrifuge type.

The sigma concept indexes the size of centrifuges based solely on sedimentation performance. Other criteria and limitations must also be considered. These limitations most often involve the ability of the centrifuge to handle solids once they are sedimented. This may require knowledge of solids residence time, G-level, solids transportability (conveyability or flowability), compressibility and recognition of the limits on torque and solids loading.

Filtering Centrifuges

Ideal System

Filtration systems, centrifugal or otherwise, usually conform to the same fundamental relationship, which is defined as:

$$Q/A = P/R \qquad [38]$$

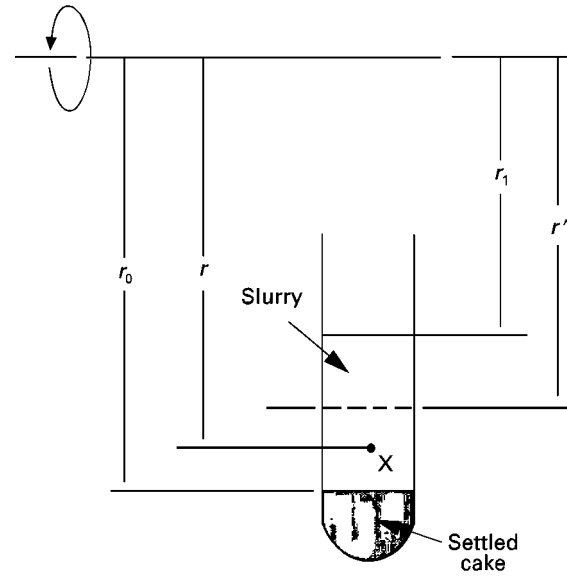

Figure 6 Bottle centrifuge (X represents the initial position).

where Q is the volumetric flow rate, and A is the cross-sectional area of the medium. P is the driving force, which is dependent on the equipment chosen. R is the resistance that depends on the materials being processed. Q/A, not surprisingly, is analogous to Q/Σ. The driving force (P) is proportional to the G-level. The bulk of the discussion revolves around how to determine the cake resistance (R).

Cake Drainage

The theory covering drainage in a packed bed is incomplete, especially when a centrifugal field is applied. It is an exceptional case when a theoretical solution might be applicable. Most of the work in this area involves numerical integration of experimental data if available, empirical rules, and simplifying assumptions. Liquid is held in the cake by various forces. Several flow mechanisms are proposed for liquid removal. In a centrifugal field, the acceleration is a function of radius from the centre of rotation which might cause changes in the packing of the bed and the acceleration of the liquid. The effective force on the particle is proportional to $(\rho_p - \rho_l)$, as the liquid in the bed drains $\rho_l \to 0$, so that the effective force on the particle changes. It is difficult to construct a useful theoretical model under these conditions that might be used in the absence of empirical data.

During cake deposition, a continuous head of liquid ranging in composition from that of the feed to an essentially clarified supernate may exist over the cake bed. If the cakes are slow draining a layer of clarified liquid may exist over the cake bed even after the feed is stopped. Draining under these conditions requires continuous flow through the cake. These interstitial spaces are assumed to be full. When a layer of free liquid no longer exists above the cake, the free liquid surface moves through the cake to an equilibrium position at the capillary height, leaving behind voids filled with gas or vapour. After bulk drainage of the larger voids, liquid still exists in the cake's upper portion in a film covering the surfaces of the solids and in partially filled voids having restricted outlets. Eventually, some of this liquid flows as a film to the continuous liquid layer at the capillary height. Typical drain time after the disappearance of a free liquid head above the cake is shown in **Figure 7**. Some essentially undrainable liquid exists within the body of each particle or in fine deep pores without free access to the surface except possibly by diffusion. This last type of liquid might be removed by evaporation or possibly by displacement with another liquid but cannot be removed mechanically by either a gravitational or centrifugal field. Treatment of empirical data is discussed in the literature.

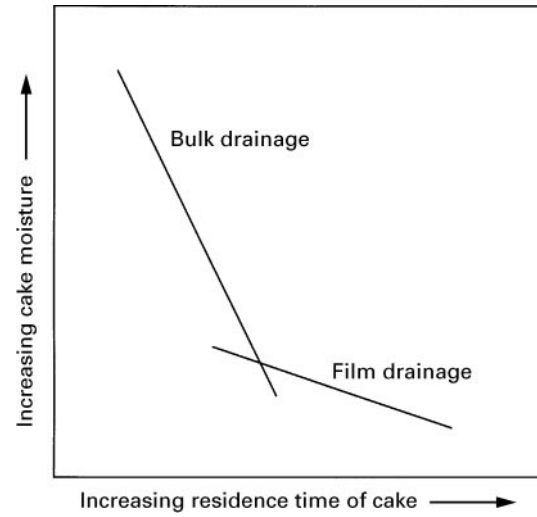

Figure 7 Typical drain time.

See also: **II / Centrifugation:** Large-Scale Centrifugation.

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